

UTILIZATION OF WASTE

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GLASS CRYSTAL MATERIALS MADE FROM MINERAL AND TECHNOGENIC FEEDSTOCK FROM KARELIA

V. P. Il'ina¹Translated from *Steklo i Keramika*, No. 9, pp. 20–23, September, 2007.

Facing and decorative glass crystal materials were developed from mineral feedstock and technogenic wastes. The effect of the components present in the mineral feedstock in liquation and crystallization of the glasses was investigated. The materials obtained can be used in construction for facing walls.

Silicate rocks and industrial technogenic wastes are widely used to make opacified glass and glass crystal facing and decorative articles. Such raw materials usually have a heterogeneous composition with predominance of one or two components that will significantly affect crystallization and the physicomachanical properties of the articles. Such components include the iron, sodium, and potassium oxides present in wastes from concentration of feldspar rocks. In addition, such components as chromium, manganese, etc., present in small amounts in chromite or manganese ore wastes, and phosphoric anhydride and fluorine contained in apatite concentrate initiate crystallization of glass in production of glass crystal materials [1]. The compositions of the glasses obtained from mining industry wastes have been investigated very little.

¹ Institute of Geology, Karelian Science Center, Russian Academy of Sciences, Petrozavodsk, Russia.

We studied the effect of the components present in mineral and technogenic feedstock on liquation and crystallization processes and consequently on the structure and properties of glass crystal materials.

Glass crystal materials were made from local readily available feedstock: Tikshozerskoe carbonatite, quartz-feldspar rock concentration wastes — Kostomuksha hälleflintas, apatite concentrate, wastes from concentration of Aganozerskoe chromite ore (Pudozhsky Region). The chemical composition of the raw materials is shown in Table 1.

The mineral composition of the Tikshozerskoe carbonatites was (%):² 70–75 calcite, 9–11 apatite, 4–8 micas, 4–5 magnetite. The maximum fluctuations of the P₂O₅ content were 0.5–12.6%. The average P₂O₅ content by deposit was 4.3%. The variations in the calcium content, established with the value of CO₂, varied from 4 to 35% (30% on aver-

² Here and below: mass content.

TABLE 1

Material	Mass content, %										
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	MgO	CaO	MnO	Na ₂ O	K ₂ O	calcination loss
Carbonatite	4.41	0.13	0.85	5.82	4.15	3.37	47.00	0.18	0.15	0.49	33.45
Hälleflinta concentration wastes	61.20	0.28	16.60	8.70	—	2.50	2.80	0.14	3.82	1.55	2.10
Apatite concentrate*	0.54	—	0.09	0.02	39.10	0.01	50.90	—	1.25	—	5.61
Chromite ore wastes	31.90	< 0.01	0.39	15.25	18.50**	22.60	5.72	0.10	0.18	0.01	3.82

* The apatite concentrate contained 2.48% F.

** Cr₂O₃.

age by area). The carbonatites were investigated as feedstock for production of lime binder, cement, fertilizers, and for other products.

The wastes from concentration of hälleflinta are formed in production of iron-free quartz-feldspar concentrate ($0.2\% \text{Fe}_2\text{O}_3$) for household porcelain and glazes. The wastes were finely dispersed with a high iron oxide content ($8.7\% \text{Fe}_2\text{O}_3$).

The apatite concentrate with a high content of P_2O_5 and CaO was used as a glass crystallization stimulator. In the glass melt, P_2O_5 causes stratification and microcrystallization on subsequent heating.

Aganozersky chromite ores contain $27.5\% \text{Cr}_2\text{O}_3$ on average and after concentration, the amount of chromium oxide reaches $47.85 - 48.94\%$. The yield of concentration "tails" is $60 - 75\%$ for a $10 - 18\% \text{Cr}_2\text{O}_3$ content. The wastes from concentration of chromite ore were used as a glass crystallization initiator in [2].

The technology for fabrication of glass crystal materials included grinding and careful mixing of the components. The batch was melted in a Silit furnace in crucibles at a temperature of $1320 - 1380^\circ\text{C}$ and $1.5 - 2$ h holding at this temperature. The glass melt was poured into metal molds at a temperature of $1200 - 1100^\circ\text{C}$ and fired at $600 - 650^\circ\text{C}$. The method of fabricating sitals based on use of controlled crystallization of silicate glass was used for glasses made from hälleflinta concentration wastes.

The flexural and compressive strength was measured on a R-5 tensile-testing machine with a load rate of 100 mm/min . The chemical stability of the glasses was determined according to GOST 101340-3-82. The CLTE was measured on $50 \times 4 \times 4 \text{ mm}$ samples of opacified glass on a DKV-5AM dilatometer (GOST 10978-83).

The phase composition and structure of the glasses were investigated with the data from x-ray phase analysis by the method of small-angle x-ray scattering and a microprobe analysis was also conducted on an INCa – Energy electron-probe microanalyzer.

Glasses made from carbonatite and apatite concentrate with the following ratio of components (%) were used to study the structure and properties: $38.73 - 48.28 \text{ SiO}_2$, $24.58 - 36.99 \text{ CaO}$, $5.87 - 9.35 \text{ Al}_2\text{O}_3$, $3.48 - 8.78 \text{ Na}_2\text{O}$, $4.11 - 12.50 \text{ P}_2\text{O}_5$, $1.40 - 2.02 \text{ MgO}$, $1.90 - 5.62 \text{ Fe}_2\text{O}_3$, $0.50 - 2.00 \text{ F}$, $0.10 - 0.28 \text{ K}_2\text{O}$, $0.01 - 0.28 \text{ TiO}_2$, $0.01 - 0.10 \text{ MnO}$, $0.01 - 0.10 \text{ Cr}_2\text{O}_3$ (FG Patent No. 2059580) and glasses made from hälleflinta wastes with addition of dolomite, chromite concentration wastes, and manganese ore containing (%): $61.50 - 66.00 \text{ SiO}_2$, $0.05 - 0.15 \text{ TiO}_2$, $14.50 - 17.00 \text{ Al}_2\text{O}_3$, $0.50 - 2.00 \text{ Fe}_2\text{O}_3$, $0.50 - 2.00 \text{ FeO}$, $2.50 - 8.00 \text{ MgO}$, $5.00 - 8.00 \text{ CaO}$, $4.00 - 5.50 \text{ Na}_2\text{O}$, $0.35 - 1.00 \text{ K}_2\text{O}$, $0.05 - 3.00 \text{ MnO}$, $0.50 - 2.00 \text{ Cr}_2\text{O}_3$ [3].

The effect of the components present in the mineral feed stock: P_2O_5 , F, Cr_2O_3 , MnO, and Fe_2O_3 , was investigated to stimulate bulk crystallization and liquation of the glasses. The combined effect of Cr_2O_3 , MnO, and Fe_2O_3 in addition to chromite and manganese ore wastes was effective for

microcrystallization of the glasses based on hälleflinta concentration wastes. These glasses crystallized in bulk during firing, since crystal growth took place at a relatively large number of crystallization centers uniformly distributed over the entire volume of the glass. A large amount of iron oxide in the wastes increased the crystallization temperature range ($800 - 1000^\circ\text{C}$) and ensured formation of a more homogeneous fine crystal structure. The chromium oxide present in chromite ore wastes played the role of an initiating additive that caused formation of chromium-oxide groups which separated from the glass in the form of a crystalline phase.

According to the findings of x-ray phase analysis, the crystalline phase of glass made from hälleflinta concentration wastes is represented by the spinel $(\text{Mn}, \text{Fe}) \cdot (\text{Cr}, \text{Al})_2\text{O}_4$. The mineral composition of hälleflinta intensifies glass formation due to the low-melting eutectics formed by finely disperse quartz and albite, decreasing the crystallization temperature of the glasses.

The heat treatment regime for the glasses was selected based on the DTA data. The temperature of the first stage of heat treatment (possible formation of crystallization centers) was equal to 600°C with holding for 1 h. Heat treatment in the second stage (crystallization of the basic mineral phase) was conducted at 850 and 950°C with holding for $1 - 2$ h. Tiles made from this glass had a monochromatic shiny surface and after second-stage heat treatment, a glass crystal material with a surface simulating natural stone of the granite type was obtained.

Glasses with carbonatite and apatite concentrate consist of a crystalline phase represented by β -wollastonite and a phosphate-silicate glass phase. Tiles made of opacified glass based on carbonatite have a variable color scale: navy blue and dark blue overflows on a light beige-light blue background.

The studies of the microstructure of these glass crystal materials by small-angle x-ray scattering (Guinnet method) were conducted at the Kuusinen Petrozavodsk State University. Three size fractions of inhomogeneities — pores — were found in glasses with different initiating additives (\AA): $(150 - 200) \pm 10$, 50 ± 5 , and 6 ± 2 . Oblique pictures of the samples with respect to the primary beam showed that the form of the electron density inhomogeneities changed from equiaxial in the initial glasses to nonequiaxial in the glasses undergoing heat treatment. This type of change in the morphology of the glasses in heat treatment took place as a result of their crystallization and formation of β -wollastonite phases in glasses of the carbonatite and $(\text{Mn}, \text{Fe}) \cdot (\text{Cr}, \text{Al})_2\text{O}_4$ spinel type based on hälleflinta concentration wastes, which appeared as a result of annealing at $600 - 650^\circ\text{C}$. The reflections from β -wollastonite and the spinel were characterized by a significant integral half-width, which indicates their fine dispersion.

The relative volume occupied by electron density inhomogeneities (pores) varied from 3 to 12% as a function of the concentration and type of crystallization initiator

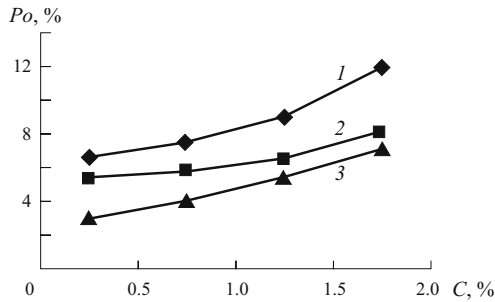


Fig. 1. Change in porosity as a function of the content of initiating components in the initial glasses: 1) P₂O₅; 2) F; 3) Cr₂O₃, MnO, Fe₂O₃.

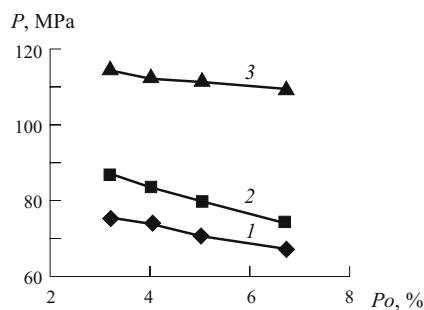


Fig. 2. Change in the mechanical strength of glasses with initiating components after heat treatment as a function of their porosity. Designations the same as in Fig. 1.

(Fig. 1). Glasses with carbonatite, where apatite acts as opacifier, were more porous. These glasses had lower mechanical strength after heat treatment at 650°C in comparison to the glasses with hälleflinta, in which Cr₂O₃, MnO, and Fe₂O₃ were the initiators (Fig. 2).

It was found that after heat treatment, the contribution of electron density inhomogeneities of minimum size to the intensity of small-angle x-ray scattering (SAX) decreased due to a decrease in their number. The contribution of inhomogeneities of the medium-size fraction to the SAX intensity almost did not change after heat treatment. The fraction of the SAX intensity for scattering by inhomogeneities of the

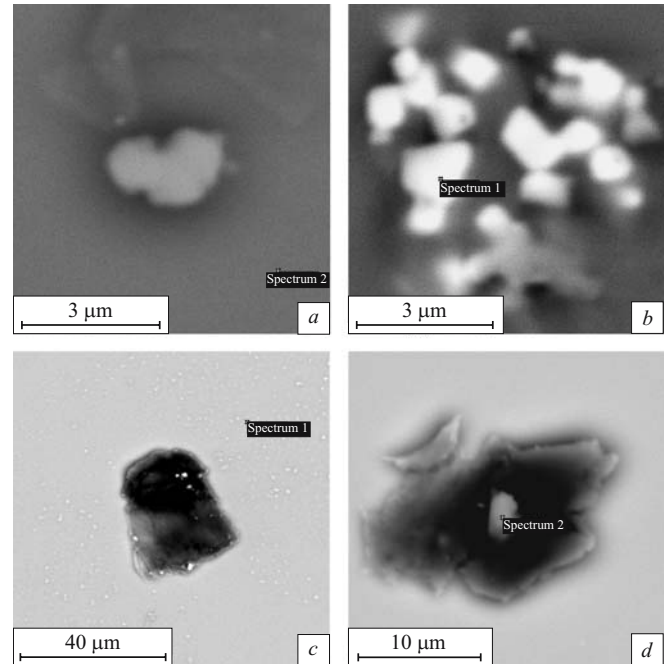


Fig. 3. Electron image of the glass surface with (Mn, Fe) · (Cr, Al)₂O₄ spinel (a, b) and β-wollastonite (c, d).

largest size fraction after annealing tended to decrease due to a change in the shape of the scattering center. The volume of the inhomogeneities of the large size fraction decreased by 3.5 times in comparison to the initial state.

The volume of inhomogeneities of large fractions almost spherical in shape in the initial glasses was thus equal to: $V_{\text{inhom.sp}} = 14 \times 10^6 \text{ Å}^3$; after heat treatment, the volume of inhomogeneities having an other than spherical (cylindrical) shape was $V_{\text{inhom.c}} = 4 \times 10^6 \text{ Å}^3$.

The chemical composition (Table 2) and structure (Fig. 3) of the glass crystal materials were determined on an INCa – Energy electron probe microanalyzer. The chemical composition of the glass crystal materials at different points on the surface (see Table 2) based on the number of dominant components indicated the content of the silicate glass phase (see Fig. 3a) and (Mn, Fe) · (Cr, Al)₂O₄ spinel (see Fig. 3b),

TABLE 2

Glass	Mass content, %									
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Cr ₂ O ₃	FeO	MnO	P ₂ O ₅
Fig. 3a Spectrum 2	66.31	15.17	4.85	0.65	1.72	7.56	–	0.60	3.14	–
Fig. 3b Spectrum 1	4.19	4.19	0.79	–	8.96	0.67	65.83	2.96	12.41	–
Fig. 3c Spectrum 1	47.09	11.64	5.02	0.40	1.50	23.13	–	1.76	–	9.46
Fig. 3d Spectrum 2	36.87	13.60	2.92	1.56	27.13	6.62	–	7.44	–	3.86

TABLE 3

Index	Glass crystal material based on	
	carbonatite	hällflinta
Specific mass, g/cm ³	2.73	3.08
Melting temperature, °C	1320	1380
CLTE, 10 ⁻⁷ K ⁻¹	95.1	58.9
Strength, MPa:		
flexural	76	120
compressive	180	810
Chemical stability, %, with respect to:		
H ₂ SO ₄	99.7	99.7
2 N HCl	99.8	99.8
6 N NaOH	97.1	98.9
H ₂ O	99.8	99.9

phosphate-silicate glass phase, β -wollastonite, β -CaSiO₃ (see Fig. 3c), and clinoenstatite, MgSiO₃ (see Fig. 3d).

The structure of the glass crystal materials based on mineral and technogenic feedstock in which the components act as crystallization initiators are thus characterized by inhomo-

geneity and microporosity which are a function of the type and concentration of initiating components. Opacified glasses based on carbonatite and apatite are distinguished by greater microporosity than glasses based on feldspar feedstock (hällflinta) and chromite ore concentration wastes. Chromite ore concentration wastes are an effective catalyst of crystallization for glasses, increase the mechanical strength, and improve the decorative properties of glass crystal materials.

The properties of the glass crystal materials obtained are reported in Table 3.

The materials have not only good decorative properties but also high mechanical strength and chemical stability. They can be used in construction for wall facing.

REFERENCES

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